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Journal

Nature Catalysis, 2(1)

ISSN

2520-1158

Authors

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Publication Date

2019

DOI

10.1038/s41929-018-0201-7

Peer reviewed

Evidence for product specific active sites on oxide-derived Cu catalysts for electrochemical CO₂ reduction

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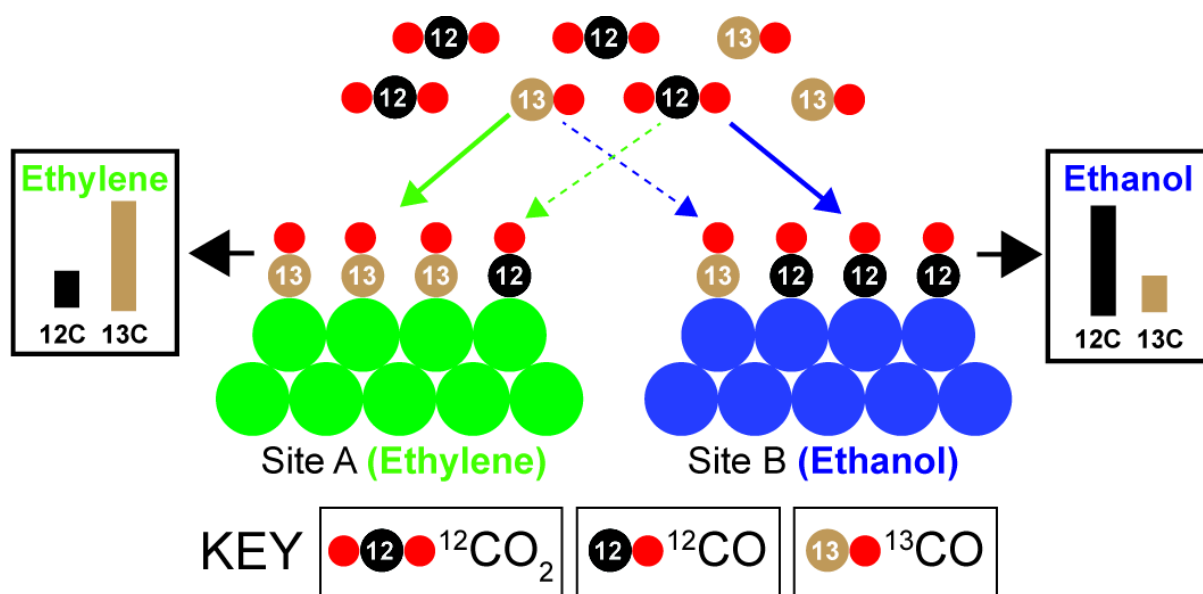
CO₂ electroreduction in aqueous media using Cu catalysts can generate many different C₂/C₃ products, leading to the question whether all products are generated from the same types of active sites or if product specific active sites are responsible for making certain products. Here, by reducing mixtures of ¹³CO and ¹²CO₂, we show that oxide derived (OD) Cu catalysts have 3 different types of active sites for C-C coupled products, one for producing ethanol/acetate, another for ethylene and yet another for 1-propanol. In contrast, we do not find evidence of product specific sites on polycrystalline Cu and oriented (100) and (111). Analysis of the isotopic composition of the products leads to the prediction that the adsorption energy of *COOH (product of the first step of CO₂ reduction) may be a descriptor for the product selectivity of a given active site. These new insights should enable highly selective catalysts to be developed.

24 The last few decades alone have seen large increases in atmospheric
25 CO₂ concentrations, mainly due to mankind's consumption of fossil fuels
26 for energy.¹ It has been projected that global energy consumption will
27 continue to rise, leading to tripling of CO₂ emissions by 2040.¹ There is
28 therefore an urgent need to develop technologies capable of efficiently
29 harvesting and storing renewable energy to reduce our dependence on
30 fossil fuels.²

31 Electrochemical CO₂ reduction (CO₂R) in aqueous media presents an
32 attractive and viable strategy to reduce carbon emissions by directly
33 converting CO₂ into valuable hydrocarbons and oxygenates such as
34 ethylene and ethanol.^{3,4} To date, Cu remains the most promising catalyst
35 capable of driving this conversion process at reasonable current
36 densities.^{5,6} While methane, ethylene, and ethanol are the major products,
37 up to 18 different possible products can be produced.⁷⁻⁹ It is commonly
38 accepted that except for formate, CO₂R on Cu is initiated by reducing CO₂
39 to adsorbed CO (*CO).¹⁰⁻¹³ Further protonation of *CO results in methane/
40 methanol formation (C₁ pathway) or *CO can couple with another *CO (C-C
41 coupling), leading to C₂/C₃ products such as ethylene and 1-propanol.¹⁴⁻¹⁶
42 However, although there have been intriguing reports of selective
43 ethylene production under a certain range of conditions and at high
44 current densities^{17,18}, it has been experimentally difficult to control
45 selectivity to a given C₂ or C₃ product. To further improve catalyst
46 performance and selectivity, it is crucial to first identify and understand
47 the nature of the active sites that are present on Cu electrocatalysts. A
48 related and important question is whether all products are produced from
49 the same active sites or if specific active sites are responsible for
50 generating a given product. In other words, are there product specific
51 active sites that mostly generate only one product?

52 We reasoned that it would be possible to answer these critical questions
53 by performing electroreduction of a mixture of ¹³CO and ¹²CO₂. To explain
54 our rationale, consider a hypothetical catalyst that possesses only 2 types
55 of active sites for C₂ production (see Fig. 1). We assume that one site (A)
56 is selective for ethylene while the other (B) is selective for ethanol.

57 Because their catalytic properties are different, we would expect that the
 58 adsorption energies of intermediates, often used as a descriptor for
 59 catalytic activity,¹⁹⁻²¹ should also be different on the two sites. Due to the
 60 difference in intermediate adsorption energies, we would naturally expect
 61 that the turn over frequencies for generating these intermediates will be
 62 different. As a specific example, the rate of the initial step of CO₂R,
 63 converting CO₂ to *CO, will be different on the two sites. As a result, if we
 64 were to reduce a mixture of ¹³CO and ¹²CO₂, the turn over frequency for
 65 ¹²CO₂ reduction to *¹²CO should be active site dependent, resulting in sites
 66 A and B having different probabilities of being occupied by *¹²CO vs *¹³CO.
 67 In this case, we assume that the turn over frequency of ¹²CO₂ reduction to
 68 *¹²CO is higher for site B, leading to a higher (lower) probability of *¹²CO
 69 (*¹³CO) on this site.



77 In the next electrocatalytic step, C-C coupling between the *CO on the
 78 sites, followed by a series of proton-coupled electron transfers and
 79 dehydration steps^{16,22-24}, results in formation of ethylene (for site A) and
 80 ethanol (for site B). Crucially, the isotopic composition of the products will
 81 be different: in this hypothetical case, ethylene will have more ¹³C than

ethanol. More generally, this analysis shows that if a mixture of ^{13}CO and $^{12}\text{CO}_2$ is reduced, the isotopic composition of the C-C coupled products will serve as a fingerprint of the active sites which produced them. That is, if two C-C coupled products have different isotopic compositions, then they have been produced by different types of active sites. On the other hand, if the catalyst does not have product specific active sites, then all products should have similar isotopic compositions.

In this work, we apply this isotope labelling concept to analyse the active sites on oxide-derived (OD) Cu catalysts. Such catalysts are typically prepared by oxidation of a Cu foil/film, followed by reduction to its metallic state.²⁵⁻²⁹ This class of catalysts, originally reported by Kanan and co-workers, is of significant interest because they have shown dramatically reduced overpotentials for the reduction of CO to oxygenate products (e.g. ethanol) with high faradaic efficiencies.^{27,30} Furthermore, work from many research groups have shown that these catalysts exhibit enhanced selectivity for reducing CO_2 to C_2/C_3 products, whilst suppressing the formation of C_1 products.^{25,26,28,31-33}

There have been a number of studies aimed at identifying the active sites responsible for the unique catalytic properties of OD Cu. Chorkendorff and co-workers used temperature programmed desorption to detect strong CO binding sites that are not present on polycrystalline Cu.³⁴ They posited that these strong binding sites could be the grain boundaries observed in their OD Cu catalysts. In related work, Kanan and co-workers demonstrated that grain boundaries are the active sites for reduction of CO to C_2/C_3 products.^{34,35} However, it is not known whether all the grain boundaries are active or if only the ones with specific structures are responsible for generating most of the products.

The objective of this work is to determine if product specific active sites are responsible for the superior C_2/C_3 selectivity of OD Cu. Evidence of product specific sites will motivate future studies to understand how each of these different active sites work and to develop methods for building specific types of product specific sites into a single structure, both of which could lead to CO_2R catalysts with greatly improved product

selectivity. Indeed, we have discovered that OD Cu has at least three types of active sites which selectively produce ethylene, ethanol/acetate and 1-propanol, respectively. In contrast, polycrystalline Cu and as well as Cu (100) and Cu (111) oriented surfaces do not appear to have product specific active sites.

Results

Reduction of ^{13}CO and $^{12}\text{CO}_2$ mixtures. Due to the large differences in the aqueous solubility between ^{13}CO (1 mM) and $^{12}\text{CO}_2$ (33.4 mM), selecting their ratio to achieve a given $^{12}\text{CO}:^{13}\text{CO}$ surface coverage merits some discussion. Based on calculations and experiments (Supplementary Figs. 1-2), we estimated that a 70:30 ratio of ^{13}CO to $^{12}\text{CO}_2$ would allow for similar rates of $^{*13}\text{CO}$ and $^{*12}\text{CO}$ formation to occur. OD Cu catalysts were prepared according to procedures described by Kanan and co-workers²⁷ (Supplementary Figs. 3-5). Polycrystalline Cu (PC Cu) was prepared by electropolishing of Cu foil and oriented surfaces of Cu (100) and Cu (111) were fabricated using procedures developed by Jaramillo and co-workers.³⁶ Natural abundance CO_2 reduction in 0.1 M KHCO_3 with these catalysts qualitatively reproduced previously reported results (Supplementary Fig. 6 and Supplementary Figs. 8-10). Natural abundance CO reduction in 0.1 M KOH (Supplementary Fig. 7) confirmed that our OD Cu catalysts performed similarly to those reported by Kanan and co-workers.²⁷ Gas chromatography-mass spectrometry (GCMS) and ^{13}C NMR were employed to determine the isotopic composition of the gas and liquid products (see Methods and Supplementary Figs. 11-23 and Supplementary Tables 1-8 for details). For experimental validation we reduced $^{13}\text{CO}/^{12}\text{CO}$ in ratios of 1:3, 1:1 and 3:1 on the OD Cu catalyst and observed the expected statistical isotope compositions and distributions (see Supplementary Tables 9-14 for details). Throughout this work, we will refer to the isotopic composition as the fraction of ^{13}C in the product. Additionally, the ^{12}C - ^{13}C distribution, for example of ethylene, refers to the fractions of the 3 possible product variants: $^{12}\text{CH}_2^{12}\text{CH}_2$, $^{12}\text{CH}_2^{13}\text{CH}_2$ and $^{13}\text{CH}_2^{13}\text{CH}_2$.

147 Confident of our experimental and analytical methods, we proceeded to
148 carry out the reduction of the 70:30 $^{13}\text{CO}/^{12}\text{CO}_2$ gas mixture with the oxide-
149 derived Cu catalyst. Fig. 2a shows the isotopic compositions of ethylene,
150 ethanol, acetate and 1-propanol produced by OD Cu at 4 different applied
151 potentials in 0.1 M KHCO_3 electrolyte. There are a number of striking
152 findings. Firstly, regardless of the applied potential, the isotopic
153 composition (^{13}C fraction) of ethanol and acetate are identical, which
154 strongly suggests that these products are generated from the same active
155 sites. Secondly, it also appears that ethylene is produced from a different
156 set of active sites, as evidenced by its consistently higher ^{13}C fraction as
157 compared to ethanol/acetate. It is also observed that the ^{13}C fraction of
158 ethylene changes more strongly with potential compared to the other
159 products. Finally, 1-propanol also has a ^{13}C fraction that appears distinct
160 from either that of ethylene or ethanol/acetate, which means that this
161 product is generated by yet another set of active sites.

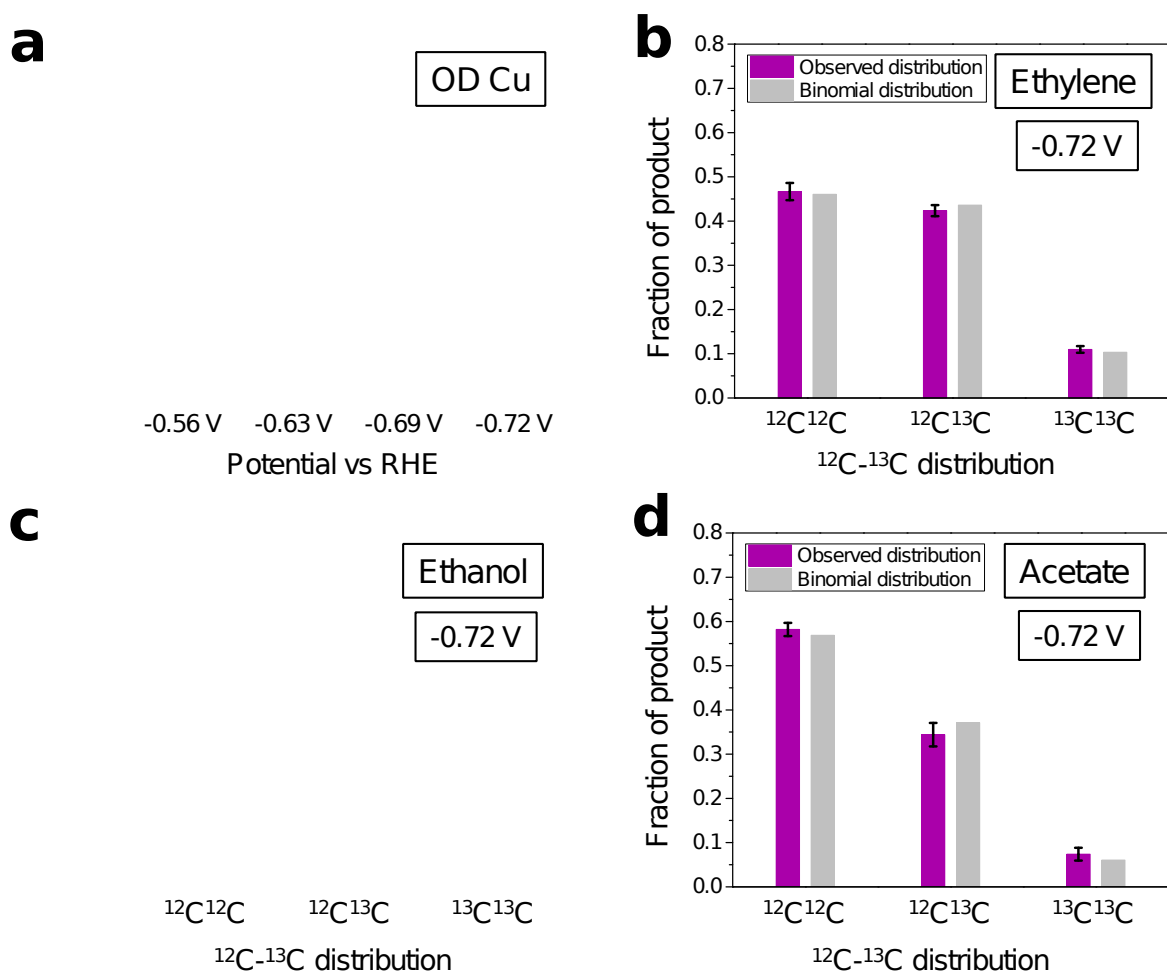


Fig. 2 | Isotopic compositions and ^{12}C - ^{13}C distributions of products generated by OD Cu. (a) Isotopic composition (in terms of the ^{13}C fraction) of ethylene, ethanol, acetate and 1-propanol produced by reduction of the $^{13}\text{CO}/^{12}\text{CO}_2$ gas mixture with OD Cu at 4 different potentials. (b), (c) and (d) are ^{12}C - ^{13}C distributions of ethylene, ethanol and acetate, respectively, at -0.72 V vs RHE. For the ^{12}C - ^{13}C distributions at other potentials, see Supplementary Fig. 27. All distributions appear to be binomial, based on comparisons with the predicted binomial distribution based on the isotopic composition (calculation details in Supplementary Tables 3-5). Faradaic efficiency and current density data are shown in Supplementary Fig. 24. Catalyst stability data are shown in Supplementary Figs. 25-26. Error bars correspond to the standard deviation of 3 independent measurements.

A more detailed analysis of the isotopic compositions provides information on the properties of the different active sites. For these 4 products, it appears that the ^{13}C fraction decreases with more negative applied overpotential. This is likely due to the fact that at more negative applied overpotentials, the turn over frequency for converting $^{12}\text{CO}_2$ to $^*\text{C}^{12}\text{O}$ on all active sites should increase, thereby increasing the probability of having a $^*\text{C}^{12}\text{O}$ vs $^*\text{C}^{13}\text{O}$ on all active sites. Since the ^{13}C fraction of ethanol/acetate is consistently lower than that of the other

181 products, it must mean that the active sites that generate these products
182 have a higher probability of having a $^{*12}\text{CO}$. Therefore, the active sites
183 that generate ethanol/acetate should have catalytic properties such that
184 they are also able to drive $^{12}\text{CO}_2$ to $^{*12}\text{CO}$ with a turnover frequency larger
185 than that of the ethylene active sites or 1-propanol active sites. Finally,
186 the stronger potential dependence of the ^{13}C fraction of ethylene implies
187 that the turn over frequency of $^{12}\text{CO}_2$ to $^{*12}\text{CO}$ should also have the largest
188 potential dependence compared to the other active sites.

189 The notion that ethylene and ethanol/acetate are formed on product
190 specific active sites on OD Cu is further supported by the binomial nature
191 of their ^{12}C - ^{13}C distributions. The ^{12}C - ^{13}C distributions for these products at
192 -0.72 V are shown in Figs. 2b-2d (see Supplementary Fig. 27 for the ^{12}C - ^{13}C
193 distributions at other potentials). As a comparison, the predicted binomial
194 distributions for each product are shown as well in each of the figures
195 (calculated based on the isotopic composition, see Supplementary Tables
196 3-5 for more details). If products were generated from multiple active
197 sites which are not product specific, we would observe that the ^{12}C - ^{13}C
198 distribution would be a superposition of multiple binomial distributions,
199 which would result in deviations from a true binomial distribution. Another
200 observation is that the observed ^{12}C - ^{13}C distributions of ethanol and
201 acetate (Figs. 2c and 2d) appear to be identical, which is further evidence
202 that these products are generated from the same active sites.

203 We have developed a multisite kinetic model which predicts product
204 isotopic distributions as a function of the selectivity of the active sites, the
205 $^{*13}\text{CO}$: $^{*12}\text{CO}$ ratio at a given site, and the number of active sites of a given
206 type and their turnover frequency (see Supplementary Figs. 28-30 and
207 Supplementary Table 15-17 for model details). The model allows
208 consideration of effects which would cause the $^{*13}\text{CO}$: $^{*12}\text{CO}$ ratio to be
209 similar for all sites such as surface diffusion of $^{*}\text{CO}$ and/or desorption and
210 readsorption events. Clearly, the fact that we see differences in isotopic
211 composition between the products means that reduction of CO to
212 products necessarily outcompetes these isotopic scrambling effects. The
213 model also shows that the sites must be substantially selective to observe

214 both differences in ^{13}C composition and a ^{12}C - ^{13}C distribution which does
215 not differ significantly from a binomial distribution.

216 Next, to determine if the existence of product specific active sites is a
217 feature of Cu electrocatalysts in general, we performed reduction of the
218 $^{13}\text{CO}/^{12}\text{CO}_2$ gas mixture with polycrystalline (PC) Cu, Cu (111) and Cu (100)
219 oriented surfaces. Fig. 3a shows the isotopic composition of the products
220 at -0.9 V vs RHE. In some cases, the isotopic compositions of acetate and
221 1-propanol could not be determined accurately as their formation rates
222 were too low. In contrast to the case for OD Cu, we observe that the
223 isotopic composition for the products generated are very similar, which
224 means that these catalysts do not have product specific active sites. In
225 Figs. 3b and 3c, the ^{12}C - ^{13}C distributions of ethylene and ethanol
226 generated by PC Cu appear to deviate slightly from the predicted binomial
227 distribution. This might suggest that PC Cu may have multiple active sites
228 which are not product specific. In this scenario, each type of active site
229 might have a different probability of $^*\text{C}^{12}\text{O}$ vs $^*\text{C}^{13}\text{O}$, which results in the
230 ^{12}C - ^{13}C distributions of the products being a superposition of a few
231 binomial distributions. To ensure that the similar isotopic compositions of
232 the products was not just a coincidence, happening only at -0.9 V vs RHE,
233 we tested Cu (100) at -0.8 V vs RHE. As expected, all products possess
234 similar isotopic compositions, albeit with higher ^{13}C fractions due to the
235 lower overpotential that was applied (Fig. 3d).

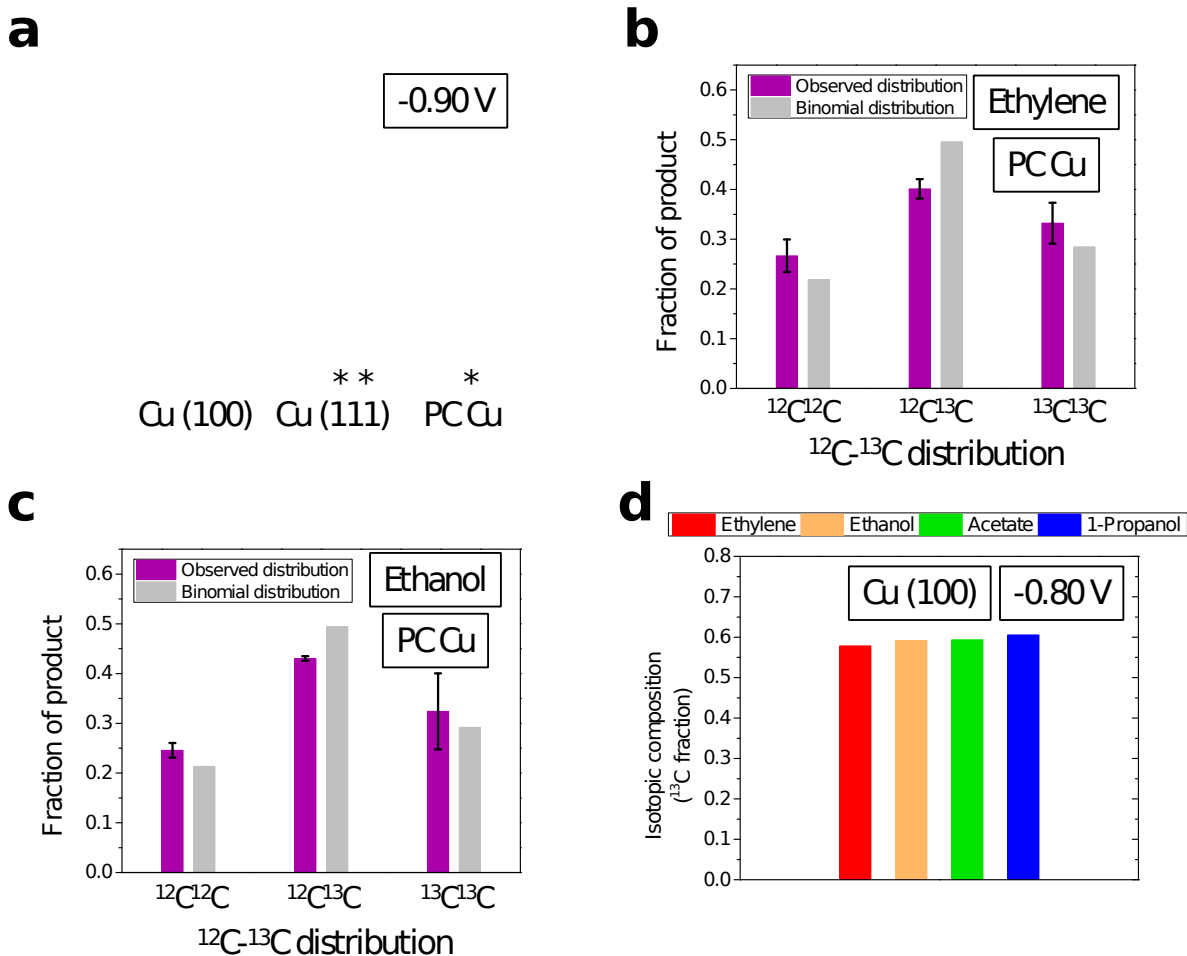


Fig. 3 | Isotopic compositions and $^{12}\text{C}^{13}\text{C}$ distributions of products generated by Cu (111), Cu (100) and PC Cu. (a) Isotopic compositions (^{13}C fraction) of products generated by Cu (100), Cu (111) and PC Cu at -0.9 V vs RHE. The * in the figure appears whenever the isotopic composition could not be determined accurately. (b) and (c) Observed and predicted binomial $^{12}\text{C}^{13}\text{C}$ distributions of ethylene and ethanol respectively for PC Cu. (d) Isotopic compositions (^{13}C fraction) of products generated by Cu (100) at -0.8 V vs RHE. $^{12}\text{C}^{13}\text{C}$ distributions for Cu (100) and Cu (111) are shown in Supplementary Fig. 31. Catalysis data is shown in Supplementary Fig. 32. Error bars correspond to the standard deviation of 3 independent measurements.

Control experiments. We performed a series of control experiments to rule out local pH, surface area/roughness and catalyst morphology effects as possible explanations for our striking findings on OD Cu. Firstly, during CO_2R the local pH of the surface rises above the bulk pH because protons from water are consumed to drive reduction of CO_2 and hydrogen evolution.^{3,37} This rise in local pH of the catalyst surface during CO_2R has been observed to suppress C_1 formation and enhance C-C coupling, thereby increasing selectivity towards C_2 products.^{17,25,29,38} For high surface area catalysts such as OD Cu, the rise in local pH is larger as compared to

planar Cu electrodes due to the larger geometric current densities.²⁶ Therefore, to minimize local pH changes, we reduced the $^{13}\text{CO}/^{12}\text{CO}_2$ gas mixture with OD Cu in a 0.1 M phosphate buffer (pH 7.2) at a potential of -0.63 V. Such a buffer has been previously shown to be effective in significantly mitigating rises in local pH.^{3,28,39} Fig. 4a shows that the isotopic compositions of ethylene, ethanol/acetate and 1-propanol remain distinct from each other in phosphate buffer, which allows us to rule out local pH effects as a possible explanation for our results.

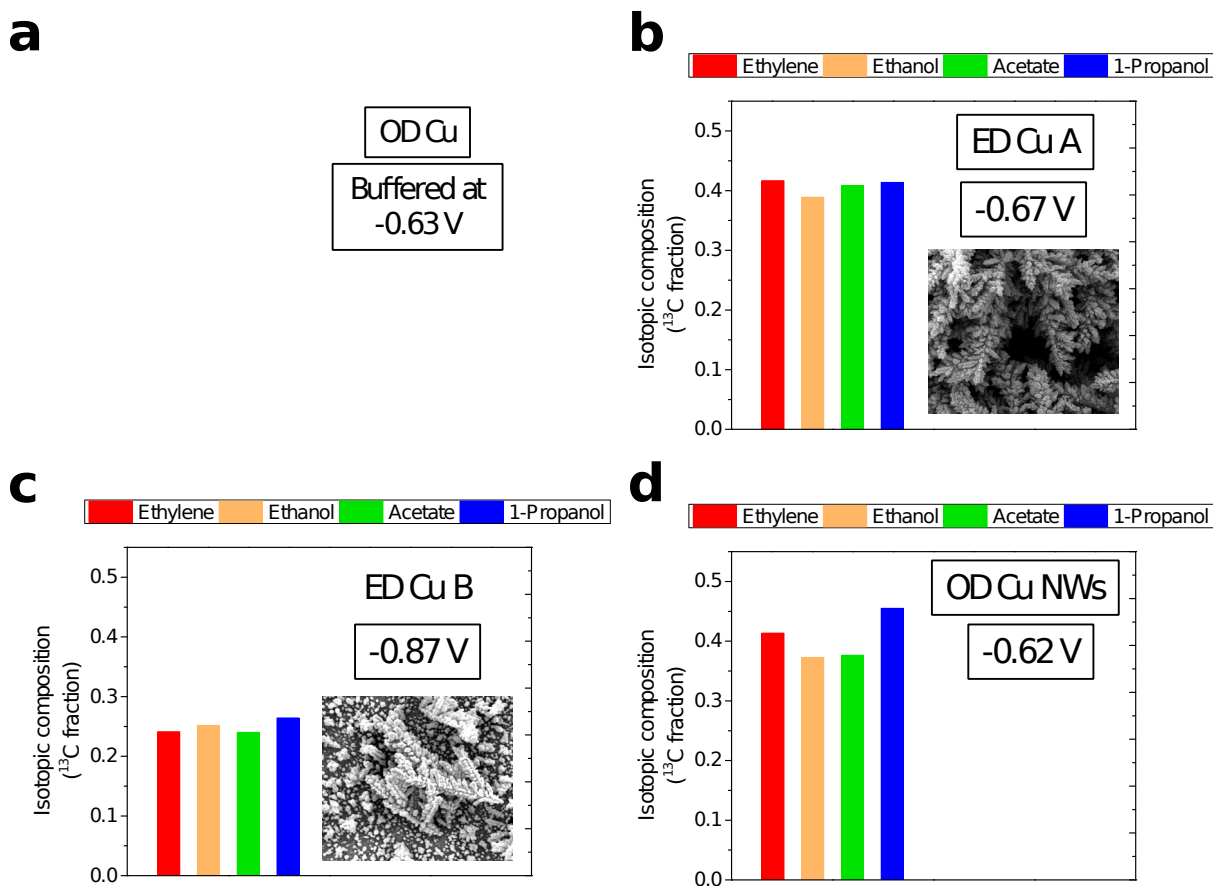


Fig. 4 | Isotopic compositions of products generated in control experiments. Isotopic compositions (^{13}C fraction) of products generated by (a) OD Cu in 0.1 M phosphate buffer at a potential of -0.63 V vs RHE, SEM image shown as inset with scale bar 1 μm . (b) ED Cu A at -0.67 V in 0.1 M KHCO_3 , SEM image shown as inset with scale bar 4 μm . (c) ED Cu B at -0.87 V in 0.1 M KHCO_3 , SEM image shown as inset with scale bar 4 μm . (d) OD Cu NWs at -0.62 V in 0.1 M KHCO_3 , SEM image shown as inset with scale bar 5 μm . Catalysis data is shown in Supplementary Fig. 37. More SEM images are available in Supplementary Figs. 34-36.

To rule out surface area/roughness effects, we tested Cu catalysts prepared by electrodeposition (ED Cu). This process generates high surface area catalysts but does not involve an oxidized Cu intermediate

(see Methods section for details). Two catalysts were prepared; ED Cu A, which has a comparable roughness factor to OD Cu (Supplementary Table 18), and ED Cu B which has a smaller roughness factor (SEM images as insets in Figs. 4b and 4c). Fig. 4b shows that products of $^{13}\text{CO}/^{12}\text{CO}_2$ reduction -0.67 V vs RHE on ED Cu A have similar isotopic compositions. Similar results were also obtained on ED Cu B, which was tested at -0.87 V vs RHE (Fig. 4c). Since we did not observe differences in isotopic composition between the products as was the case with OD Cu, we rule out surface area/roughness as a possible explanation of our results. Additionally, it is apparent that such catalyst preparation methods do not result in creation of product specific sites.

Finally, catalyst morphology has been shown to be important in determining the selectivity of Cu catalysts.⁴⁰ To explore this effect, we synthesized an oxide-derived Cu catalyst with a distinctly different morphology from OD Cu. Oxide-derived Cu nanowire (OD Cu NWs) catalysts were synthesized according to the procedure described by Smith and co-workers²⁵ with some modifications (see Methods section for details and SEM images as inset in Fig. 4d). Fig. 4d shows that the isotopic compositions of ethylene, ethanol/acetate and 1-propanol obtained by reduction of $^{13}\text{CO}/^{12}\text{CO}_2$ at -0.62 V vs RHE are also different from each other. This means that like OD Cu, OD Cu NWs also possesses product specific active sites. Similarly, we can rule out the possibility that the observed differences in isotopic composition are a result of morphology effects.

Mechanistic insights. Besides the finding that the active sites on OD Cu are product specific, several other mechanistic insights can be gained from this work. To explain oxygenate generation on Cu-based catalysts from CO_2R , several research groups have proposed that mobile nonadsorbed CO can undergo an insertion reaction with surface bound $^*\text{CH}_2$ species to form a $^*\text{COCH}_2$ intermediate.⁴¹⁻⁴³ Further reduction of $^*\text{COCH}_2$ would lead to formation of ethanol and possibly 1-propanol as well.¹³ Also, Meyer and co-workers further proposed that this $^*\text{COCH}_2$

intermediate could lead to the formation of acetate.⁴² This type of CO insertion mechanism was first proposed by Hori and co-workers, using an analogy to Fischer-Tropsch catalysis and we will refer to it as the CO insertion mechanism.¹³

Using our approach, evidence of a CO insertion mechanism could be observed in two ways. Firstly, according to the mechanism proposed by Hori, $^{12}\text{CO}_2$ would be reduced to surface bound $^*\text{^{12}CO}$ and subsequently to $^*\text{^{12}CH}_2$. Labelled CO insertion would yield a $^*\text{^{13}CO}^{12}\text{CH}_2$ intermediate, which then reduces to form ethanol, 1-propanol or acetate. Importantly, this mechanism predicts that the ^{13}C should be in the α carbon position ($-\text{CH}_2\text{OH}$) rather than the β carbon position ($-\text{CH}_3$). Similarly, for 1-propanol, ^{13}C would be in the α position ($-\text{CH}_2\text{OH}$) rather than the β ($-\text{CH}_2-$) or γ ($-\text{CH}_3$) positions. As for acetate, ^{13}C should be in the carboxyl group ($-\text{COO}^-$) rather than the α position ($-\text{CH}_3$). However, ^{13}C NMR reveals no such preference for ^{13}C to be in any of the positions relative to another (see Supplementary Figs. 39-44 for more details). Secondly, CO insertion would not produce a binomial distribution of ^{12}C and ^{13}C in the C_2 products but rather a distribution with enhanced $^{12}\text{C}^{13}\text{C}$ formation, as compared to the $^{12}\text{C}^{12}\text{C}$ or $^{13}\text{C}^{13}\text{C}$. The ^{12}C - ^{13}C distributions of ethanol or acetate do not appear to display a strong bias for formation of the $^{12}\text{C}^{13}\text{C}$ product (Figs. 2 and 3, Supplementary Figs. 27 and 31). Thus, we conclude that the CO insertion mechanism does not occur in the catalyst systems in this study.

Another interesting experimental observation is that ethanol and acetate are generated from the same active sites on OD Cu. This means that these products are likely to be linked mechanistically and thus share the same selectivity determining intermediates/steps. Indeed, ethanol and acetate have been linked closely together in previous reports. Kanan and co-workers observed substantial acetate formation at high pH during CO reduction on OD Cu, which they ascribed to attack of carbonyl-containing intermediates by OH^- .²⁷ As the increased acetate formation at high pH was accompanied by a decrease in ethanol, it can be inferred that the products share a common intermediate. As another example, Koper and co-workers proposed that Cannizzaro disproportionation of acetaldehyde

341 generates both acetate and ethanol simultaneously.⁴⁴ On the other hand,
342 our observation that ethylene and 1-propanol are generated from different
343 sites suggest that these products do not share common selectivity
344 determining intermediates/steps and branch early on after C-C coupling
345 from the ethanol/acetate pathway. Additionally, our results do not support
346 the mechanism proposed by Head-Gordon and co-workers, which places
347 acetate on the ethylene pathway rather than on the ethanol pathway.¹²

348 Additionally, our experimental observations on OD Cu may also be
349 rationalized from the point of view of scaling relations. In CO₂R,
350 intermediates bind to the surface through the C and/or the O atom.^{10,12,24,45}
351 Because of scaling relations, intermediates that bind through the C atom
352 are expected to have adsorption energies that are linearly related to each
353 other, with the same rationale applying to intermediates that bind through
354 the O atom. For ethylene selective sites, the adsorption energies of
355 intermediates must all be shifted in a way such that after C-C coupling,
356 formation of the ethylene intermediate is by far the most kinetically
357 favourable compared to the ethanol/acetate or 1-propanol intermediates.
358 On the other hand, shifting the adsorption energies of intermediates in a
359 different way could result in favouring the formation of the
360 ethanol/acetate intermediate or the 1-propanol intermediate. Recalling
361 the identification of a range of strong CO adsorption sites on OD Cu not
362 present on polycrystalline Cu by Chorkendorff and co-workers,³⁴ we find it
363 possible that these strong CO adsorption sites are associated with the
364 product specific sites that we have discovered. We further posit that these
365 sites have specific combinations of C and O adsorption energies that
366 enable them to become product specific. Kanan and co-workers have
367 shown that grain boundaries are the active sites on OD Cu for the
368 reduction of CO to C₂/C₃ products.^{34,35} We therefore think it possible that
369 the structure of each product specific active site may be a specific type of
370 grain boundary termination.

371 Another consequence of scaling relations is its effect on the formation
372 of *¹²CO from ¹²CO₂. Theoretical studies have predicted that the rate
373 limiting step of this reaction is the formation of *COOH from *CO₂.^{11,15,46}

374 Since we have consistently observed that ethanol/acetate have the
375 highest ^{12}C fractions (Fig. 2a), their active sites should have the highest
376 $^{12}\text{CO}_2$ to $^{*12}\text{CO}$ turn over frequencies. We thus posit that due to scaling
377 relations, enhancing the formation of the $^{*12}\text{COOH}$ intermediate by tuning
378 catalyst adsorption energies also enhances formation of the
379 ethanol/acetate intermediate. Additionally, ethylene and 1-propanol
380 selective sites should have different $^{*}\text{COOH}$ adsorption energies from
381 ethanol/acetate selective sites since their ^{13}C fractions depend differently
382 on the applied potential (Fig. 2a). This likely means that $^{*}\text{COOH}$ adsorption
383 energies may be a descriptor for the product selectivity of an active site.
384 Because of this, turn over frequencies for $^{12}\text{CO}_2$ and $^{*12}\text{CO}$ are active site
385 dependent, giving each site a different probability of $^{*12}\text{CO}$ vs $^{*13}\text{CO}$. This
386 gives rise to the different product isotopic compositions as we have
387 observed.

388 Finally, a theory paper published by Goddard and co-workers could
389 possibly offer some insight on our results and serve as a starting point
390 towards identifying the different active sites we have observed.⁴⁷ Using
391 molecular dynamics, they randomly generated sites on Cu nanoparticles
392 with different atomic configurations. Approximately 9% of these
393 generated sites had a larger CO binding energy than Cu (211). This would
394 seem to be consistent with the temperature programmed desorption
395 study of Chorkendorff and co-workers in which they found stronger CO
396 binding sites on OD Cu which are not present on polycrystalline Cu.³⁴
397 Among the strong CO binding sites, the theoretical study identified 2
398 atomic configurations which were proposed to be active for C-C coupling.
399 Relating these findings to our experimental work, it is conceivable that
400 some of the sites studied by Goddard and co-workers could also be
401 present on the OD Cu surface. It is possible that the differences in CO
402 binding energy for different surface configuration could be used to identify
403 C_2 and C_3 product selective sites, although more precise knowledge of the
404 selectivity determining steps would be required.

405 **Conclusions**

406 In summary, we have shown via isotope labelling that OD Cu has product
407 specific active sites for the CO₂R reaction, with one set of active sites
408 generating ethylene, another ethanol/acetate and yet another 1-propanol.
409 We reason that due to scaling relations, the rate of *COOH formation
410 (intermediate to *CO) should be different on each type of active site. This
411 means that each active site has a different probability of *¹²CO vs *¹³CO
412 and as a result, products generated from different sites possess different
413 isotopic compositions. In contrast, by performing similar experiments on
414 polycrystalline Cu, Cu (100) and Cu (111) we show that these have sites
415 that produces a mixture of C-C coupled products. Finally, our finding that
416 active sites on OD Cu are product specific should motivate future work to
417 understand these sites as well as ways to engineer specific types of sites
418 into a single structure, thereby creating catalysts with very high product
419 selectivity.

420 **Methods**

421 **Materials.** Potassium carbonate (99.995% metals basis), potassium hydroxide (99.99%
422 metals basis), ¹³C carbon monoxide (<5 atom % ¹⁸O, 99 atom % ¹³C), nitric acid (70%),
423 hydrochloric acid (37%), potassium phosphate monobasic (99.99% metals basis) and
424 potassium phosphate dibasic (99.95% metals basis) were purchased from Sigma-Aldrich.
425 Copper foil (0.1 mm thick, 99.9999%) and glassy carbon plates were purchased from Alfa
426 Aesar. Selemion AMV anionic exchange membranes were purchased from Asahi Glass
427 Co., Ltd. Si wafers of various orientations were purchased from UniversityWafer, Inc. The
428 copper sputtering target (99.999%) was purchased from Kurt J. Lesker Company. All
429 chemicals were used without further purification. Carbon dioxide (99.995%), nitrogen
430 (99.999%), argon (99.999%) and hydrogen (99.999%) were purchased from Praxair.
431 Natural abundance carbon monoxide (99.999% research purity) was purchased from
432 Matheson Tri-gas Inc. Hydrogen, argon, nitrogen and carbon dioxide gas purifiers
433 purchased from Valco Instruments Co. Inc were used on the gas feeds to the
434 electrochemical cell and gas chromatograph. 18.2 MΩ deionized (DI) water was produced
435 by a Millipore system and used for electrolyte preparation.

436 **Preparation of polycrystalline Cu (PC Cu).** Cu foil was cut into 2 cm by 2 cm square
437 pieces and then electropolished at a potential of 2V vs the counter electrode for a period
438 of 5 minutes. The counter electrode used was another Cu foil of larger dimensions (5 cm
439 by 5 cm).

440 **Preparation of oxide-derived Cu (OD Cu).** Oxide-derived Cu was prepared according
441 to the procedure developed by Kanan and co-workers.²⁷ Cu foil was first cut into 2 cm by
442 2 cm square pieces and then electropolished at a potential of 2 V vs the counter
443 electrode for a period of 5 minutes. The counter electrode used was another Cu foil of
444 larger dimensions (5 cm by 5 cm). To oxidize the surface, the Cu foil was thermally

annealed in air using a muffle furnace at a temperature of 500 °C for 1 hour. The muffle furnace was then allowed to cool to room temperature before removing the oxidized Cu foils.

Preparation of oriented Cu surfaces. Cu (100) and (111) oriented surfaces were prepared according to similar procedures as described by Jaramillo and co-workers.³⁶ Si wafers with different orientations were used as growth substrates to facilitate epitaxial growth of Cu. Cu films grown on Si (100) and (110) wafers yield Cu orientations of (100) and (111) respectively. The native oxide on the Si wafers was first removed via a HF etch and subsequent growth of the films was carried out using sputtering with an AJA International ATC Orion 5 sputtering system. In all cases, the thicknesses of the Cu films were controlled to be 200 nm thick using a quartz crystal monitor. Samples were kept in a N₂ filled glove box when not in use to minimize oxidation in ambient air. The orientations was also confirmed according to similar procedures reported by Koper and co-workers⁴⁸ as well as Yeo and co-workers.³² Briefly, this was accomplished with cyclic voltammetry in Ar sparged 0.1 M KOH solution in the potential range of -1.3V to -0.45V vs Ag/AgCl at a rate of 120 mVs⁻¹. OH⁻ adsorption and desorption peaks are unique and depend on the Cu surface and thus may be used to identify and confirm its orientation. Cyclic voltammetry was also carried out after CO reduction to confirm that loss of the surface orientation did not occur. (See Supplementary Fig. 33).

Preparation of oxide-derived Cu nanowires (OD Cu NWs). Oxide-derived nanowires were prepared according to the method described by Smith and co-workers, with some modifications.²⁵ Firstly, Cu foil was first cut into 2 cm by 2 cm square pieces and then electropolished at a potential of 2V vs the counter electrode for a period of 5 minutes. The counter electrode used was another Cu foil of larger dimensions (5 cm by 5 cm). The Cu foil was then immersed into an aqueous solution containing 0.133 M (NH₄)₂S₂O₈ and 2.667 M NaOH for 10 minutes, resulting in growth of Cu(OH)₂ nanowires on the surface. The foil was then thermally annealed in air using a muffle furnace at a temperature of 500 °C for 30 mins to convert Cu(OH)₂ to CuO. The muffle furnace was then allowed to cool to room temperature before removing the Cu foils.

Preparation of electrodeposited Cu (ED Cu A and ED Cu B). ED Cu A and ED Cu B were prepared by electrodeposition of Cu onto an electropolished Cu foil using a solution containing 0.1 M CuSO₄ adjusted to pH 1 using concentrated H₂SO₄. A constant cathodic current density of -400 mA cm⁻² was applied for 8 minutes for ED Cu A and only 2 minutes for ED Cu B. Such a procedure results in a dendritic, porous structure with a high surface area with the roughness factor increasing with increasing deposition time.

Materials characterization and electroactive surface area measurements. Scanning electron microscopy images were taken on a FEI Quanta 200 FEG scanning electron microscope using an accelerating voltage of 15 kV. X-ray diffraction patterns were obtained using a Rigaku Smartlab x-ray diffractometer.

Electroactive surface area measurements were performed according to procedures described by Nilsson and co-workers.³³ These measurements were performed in the same electrochemical cell as that for electrolysis experiments. 0.1 M KHCO₃ was used as the electrolyte and cyclic voltammetry was carried out in a region where faradaic processes do not occur. This was carried out with various scan rates and the geometric current density was plotted vs scan rate. The slope of this graph is equal to the double layer capacitance.

Electrochemical measurements. For all electrochemical measurements described in this work, a Biologic SP-300 potentiostat was used. CO reduction was carried out using a custom-made electrochemical cell made of PEEK and fitted with Teflon o-rings for chemical inertness and durability. In this cell, the working and counter electrodes are both constrained to be 1 cm² and sit parallel to each other in order to ensure a uniform

potential distribution across the working electrode surface. In all electrochemical CO₂/CO reduction experiments, glassy carbon was used as the counter electrode (anode) instead of Pt due to concerns regarding Pt dissolution.⁴⁹ In order to ensure that the electrolyte remains saturated with ¹²CO₂ and ¹³CO throughout electrolysis, these gases were continuously introduced into the electrochemical cell at a rate of 1.5 and 3.5 sccm respectively using mass-flow controllers. A custom-made glass frit fabricated by Adams & Chittenden Scientific Glass was used to disperse the gas into the electrolyte as well as provide adequate convection in the electrochemical cell.⁵⁰ Before carrying out bulk electrolysis experiments, the gas mixture was allowed to flow through the electrolyte in the cathode chamber for at least 15 minutes to ensure that the electrolyte is saturated. To separate the electrolyte in the cathode and anode chambers, a Selemion AMV anion exchange membrane was employed. Before use, the membrane was carefully rinsed with DI water. The electrolyte volume used in both the cathode and anode were 1.8 ml each. Before use in experiments, the electrochemical cell was sonicated in 20 wt.% nitric acid for 1 hour. All bulk electrolysis experiments were conducted for 70 minutes. A leak-free Ag/AgCl electrode from Innovative Instruments, Inc was employed as a reference electrode. The accuracy of this reference electrode was ensured periodically by comparison with a custom-made reversible hydrogen electrode. To convert potentials vs Ag/AgCl to the RHE scale, the following equation as used:

$$E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.197\text{ V} + 0.0591\text{ pH},$$

(1)

After saturation of the electrolyte with the gas mixture, the solution resistance was determined using potentiostatic electrochemical impedance spectroscopy (PEIS), scanning through a frequency range of 1 MHz to 10 Hz. 85% of the solution resistance was then compensated using the software and the remaining 15% was post-corrected after the experiment.

Preparation of electrolyte and product analysis. Preparation of electrolytes and product analysis was performed according to similar procedures as reported previously.²⁶

GCMS analysis of gas and liquid products. Isotopic composition of both the gas and liquid products were determined using gas chromatography-mass spectrometry (GCMS) with an Agilent 7890A GC with 5975C inert XL MSD (triple axis detector). The column used was an Agilent J&W PoraPLOT Q capillary column of length 25 m, internal diameter 0.25 mm and film thickness 8 μm (part number CP7549). Helium (99.999%) was used as the carrier gas with a flow rate of 1.0 ml/min in the column. A glass wool liner was used in the inlet, which was set to 250 °C.

For gas product analysis, 10 μl of gas was injected into the GCMS and the injection mode was split with a 1:1 ratio. For the analysis method, the selected ion monitoring (SIM) operating mode was used. Elution times of the target analytes (ethylene and ethane) were determined by injecting known standards. During the run, the operating temperature of the oven was set to 30 °C for 7.5 minutes. A bake out at 100 °C for 5 minutes was utilized at the end of each run.

For liquid product analysis, electrolyte samples were first acidified with concentrated hydrochloric acid to pH 2 to convert acetate into the acetic acid form, which is amenable to GCMS analysis. For each analysis, 0.5 μl of sample was injected and the injection mode was split with a 25:1 ratio. The selected ion monitoring (SIM) operating mode was used for liquid products. Similarly, the elution times of the target analytes (ethanol, 1-propanol and acetic acid) were determined by injecting known standards dissolved in water. During the run, the oven temperature was set to 145 °C for 10 minutes. A bake out at 200 °C for 5 minutes was utilized at the end of every run.

To ensure that the mass spectra of different products obtained with our GCMS are consistent with established databases,⁵¹ standards of natural isotopic abundances were

also injected and all mass fragments with m/z in the range 20 to 75 were scanned (see Supplementary Figs. 11-13 for more details).

Determination of the isotopic composition based on the mass spectrometry data is explained in the Supplementary Note 4.

¹³C NMR spectroscopy of liquid products. ¹³C NMR was utilized to analyze the isotopic composition of the liquid products using a Bruker Avance III 500 MHz spectrometer. 700 µl of the electrolyte with the liquid products was mixed with 35 µl of D₂O containing 10 mM DMSO and 50 mM phenol. To prevent ¹H protons from splitting the ¹³C nuclei, proton decoupling techniques were utilized. Samples were run for at least 12 hours to accumulate sufficient signal. Determination of the isotopic composition based on the NMR results is explained in Supplementary Note 5.

Data availability. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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704 20899.

705 Acknowledgements

706 This material is based upon work performed by the Joint Center for
707 Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through
708 the Office of Science of the U.S. Department of Energy under Award
709 Number DE-SC0004993. Y.L. acknowledges the support of an A*STAR
710 National Science Scholarship. We thank Aya Buckley for assistance with
711 ¹³C NMR spectroscopy and Wan Ru Leow for assistance with the creation
712 of figures.

713 **Author contributions**

714 Y.L and J.WA. conceived and designed the experiments. Y.L conducted all
715 the experimental work and analysed the data. All authors discussed the
716 results and wrote the manuscript.

717 **Competing interests**

718 The authors declare no competing interests.